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EFFECT OF PLASTIC DEFORMATION UPON COLLOIDAL CENTERS IN NaCl CRYSTAL*

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Introduction

Mollwo[1] demonstrated that crystals containing large colloids became dichromatic if the crystal is sheared plastically. E. Rohloff[2] studied the same type of dichroism in rolled specimens of silver chloride containing photolytically produced colloids of silver. We have found that the violet color of a NaCl crystal containing colloidal centers changes to deep blue and to light brown in the respective directions parallel and normal to the stress to which the crystal is subjected, and the changed colors recover to the initial violet during preservation or annealing. Now the effect of plastic deformation upon the colloidal centers in NaCl crystal has been investigated in detail by measuring the absorption spectra. The plastic deformation was carried out by die-casting with a pressure of 5,000 kg/cm^2 at room temperature.

Experimentals

Preparation of samples Colloidal centers in NaCl crystal were produced by annealing the crystal containing F-centers at 400°C for about 20 minutes and then rapidly quenched. The colloidal band had a peak at 574 ~ 578 mμ. The samples suitable for measurement were cleaved from the inner region of colored crystal.

Procedure *Exp.* (*1*) The crystal cleaved to a square plate of about 4.0 × 4.0 × 1.6 mm was deformed to a thin disk of 6 mm in diameter and 0.91 mm in thickness by the same procedure as used in the previous experiment[3]. The absorption spectra of this deformed crystal were measured in the direction parallel to the compression. *Exp.* (*2*) The crystal cleaved to a cube of about 4.7 × 4.7 × 13.0 mm was deformed to a cylindrical shape of 6 mm in diameter and about 10 mm in height by the same procedure as above, and then a cube of about 3 × 3 × 3 mm which has surfaces parallel and normal to the compression

* *This investigation has been done by F. Okamoto, being in the postgraduate course, under the direction of Prof. R. Kiyama.*

1) E. Mollwo, *Nachr. Akad. Wiss. Göttingen*, **1932**, 254 (1932)
2) E. Rohloff, *Z. Physik*, **132**, 643 (1952)
3) R. Kiyama and F. Okamoto, *This Journal*, **25**, 1 (1955)

was cut from the inner region of the cylindrical deformed crystal. The absorption spectra of this crystal were measured in the direction parallel and normal to the compression respectively.

The absorption measurements were carried out, over the wavelength range from 350 to 1100 mμ at room temperature, on each step of the successive treatments as follows: (i) immediately after plastic deformation, (ii) after preservation in the dark and (iii) after annealing at 100 ~ 200°C for 10 ~ 20 minutes. In these absorption measurements the deformed uncolored crystals were used as blank crystal.

Results

Changes of the absorption spectrum in the direction parallel to the compression The peak of the colloidal band shifted from 574 to 610 mμ accompanying the broadening of the band width and the decrease of the band height when the crystal was deformed in the dark (curve 2 in Fig. 1). This crystal being preserved in the dark for one day and further two days, the peak wavelength shifted from 610 to 604 and 602 mμ respectively, accompanying the reduction of the band width and the increase of the band height (curves 3 and 4). The shift of the peak wavelength could not be detected by further three days preservation (curve 5). When this crystal was annealed in the dark at 100°C for 20 minutes, the peak wavelength shifted from 602 to 579 mμ accompanying the reduction of the band width and the increase of the band height (curve 6). Further, the peak wavelength shifted to 576 mμ and F-band was formed by annealing the crystal at

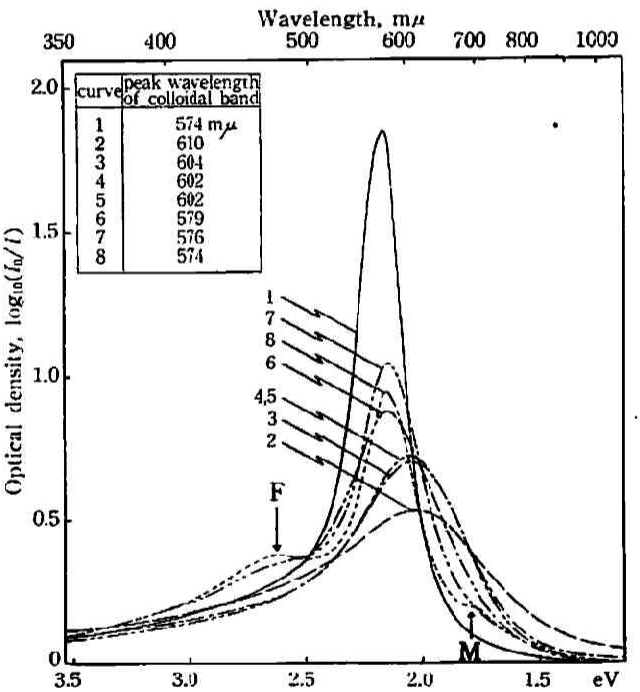

Fig. 1 Changes of the absorption spectrum of colloidal centers in NaCl crystal after plastic deformation
Measurements in the direction parallel to the compression
Crystal thickness=0.91 mm

curve 1 : absorption spectrum of the crystal previous to plastic deformation
2 : immediately after plastic deformation in the dark
3 : after 1 day preservation in the dark
4 : after further 2 days preservation
5 : after further 3 days preservation
6 : after 20 minutes annealing at 100°C
7 : after further 20 minutes annealing at 150°C
8 : after further 10 minutes annealing at 200°C

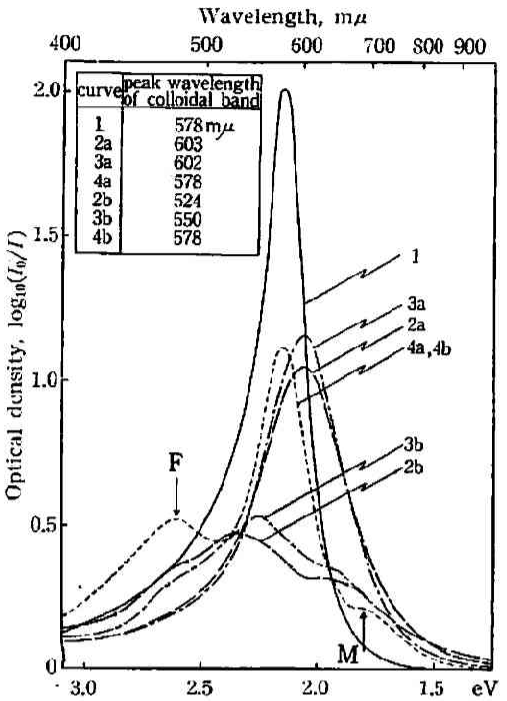

Fig. 2 Changes of the absorption spectrum of colloidal centers in NaCl crystal after plastic deformation

Measurements in the respective directions parallel and normal to the compression

Crystal thickness=about 3mm

curve 1 : absorption spectrum of the crystal previous to plastic deformation

2a and 2b : immediately after plastic deformation in the dark

3a and 3b : after 3 days preservation in the dark

4a and 4b : after 10 minutes annealing at 200°C

a, b indicate the measurements in the directions parallel and normal to the compression respectively.

150°C for 20 minutes (curve 7). This crystal being annealed at 200°C for 10 minutes, the peak wavelength returned to 574 mμ of the initial location. At the same time the increase of the F-band and the formation of M-band were observed (curve 8)

Changes of the absorption spectrum in the respective directions parallel and normal to the compression The peak wavelength of the colloidal band shifted from initial peak (578 mμ) to long wavelength side (603 mμ) and to short wavelength side (524 mμ) for measurements in the directions parallel and normal to the compression respectively, accompanying the broadening of the band width and the decrease of the band height when the crystal was deformed in the dark (curves 2a and 2b in Fig. 2). In this case it is a remarkable feature that the absorption curve 2a is simple but the curve 2b is broad and complex. These shifted band peaks had a tendency to return toward the initial location during preservation in the dark (curves 3a and 3b). When this crystal was annealed at 200°C for 10 minutes, both absorption curves 3a and 3b became an identical shape and the peak wavelength returned to 578 mμ of the initial location accompanying the reduction of the band width and the increase of the band height. At the same time F- and M-bands were formed (curves 4a and 4b).

Considerations

Exp. (*2*) which contains the treatment of cutting of the deformed crystal may be less quantitative than *Exp.* (*1*) because of the difficulty in exact cutting. However, the result of *Exp.* (*2*) in the direction parallel to the compression is qualitatively identical with the result of *Exp.* (*1*). This fact indicates that the result of *Exp.* (*2*) is sufficient for the qualitative discussion.

The simple bell-shaped absorption band which has a band peak at longer wavelength side was obtained by the measurement in the direction parallel to the compression, and the broad and complex absorption band which has a band peak at shorter wavelength side was obtained by the measurement in the direction normal to the compression. The results indicate that all the spherical colloidal particles are deformed to essentially the same ellipsoidal shape as shown in Fig. 3 when the crystal is subjected to uniaxial compression. The return of the shifted band peaks toward the initial peak

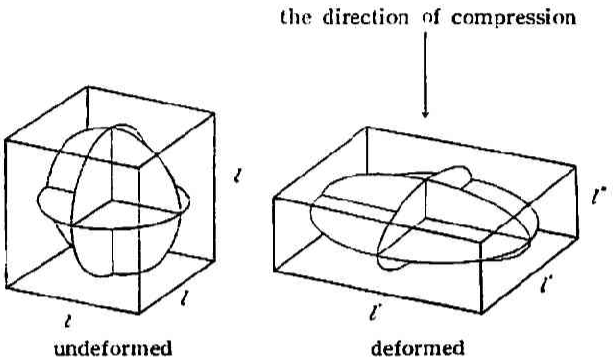

Fig. 3 The deformation of the spherical colloidal particles to the ellipsoid of rotation by uniaxial compression

during preservation is ascribed to the recovery of the deformed colloidal particles. Annealing accelerates the recovery. The result that part of the colloidal centers in the deformed crystal is converted into F- and M-bands at low temperatures, such as 150 ~ 200°C, may be due to the large density of positive- and negative-ion vacancies which are formed during plastic flow[4,5] and the existence of the deformed unstable colloidal particles.

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4) F. Seitz, *Phys. Rev.*, **80**, 239 (1950)
5) F. Seitz, *Rev. Mod. Phys.*, **26**, 25 (1954)